

CLAIMS

I claim:

1. A method of treating a liquid stream which contains impurities in limited amounts with a solid adsorbent having an affinity for the impurities compared with other components in the liquid to reduce the impurities significantly for the adsorber-treated product with the following steps:

providing a liquid fresh feedstream to an adsorber suitably cooled and suitably free from agents which might degrade the impurity removal performance after long term regeneration;

providing a porous, particulate adsorbent within a 8 to 48 Tyler mesh range and in a suitably narrow fraction such that size segregation is acceptable when subject to fluidization with bed expansions no greater than 10 percent with the liquid feedstream or liquid effluent from preceding adsorption stages;

providing an adsorption section consisting of liquid fluidized stages with a bottom inlet and an upper outlet in the adsorber vessel and the same if more than one adsorber vessel;

introducing an adsorbent stream into an upper part of a last adsorption stage to countercurrent contact the said liquid stream that flows upward from a preceding adsorption stage until the said liquid fresh feedstream enters a fresh feed adsorption stage;

withdrawing spent adsorbent as a slurry near an inlet distributor of the fresh feed adsorption stage to proceed to a liquid-solid separator that separates liquid forming the slurry for return as liquid to the adsorption feed stage, whereas the solids separated enter a regeneration section that has at least two desorption zones and a cool-down zone for the regeneration of the spent adsorbent stream;

providing the regeneration section with two or more desorption zones which first continuously desorb a significant portion of the desired liquid product initially in spent adsorbent pores of the adsorbent by recirculating gas after cooling and condensing most of the liquid released, with impurity concentration lower than that of the fresh feed, by stripping and heating with this recirculated gas with suitable

makeup gas to a higher temperature than the solids leaving a recycle liquid desorption zone, but significantly lower in temperature than that used for heated gas that enters a final desorption zone and which sufficiently removes the impurities from the solids as a concentrated impurity stream;

introducing desorbed adsorbents from the final desorption zone into the cool-down zone of the regenerator;

introducing a reactivating gas sufficiently free from any agents that might interfere with the desired adsorption of impurities to accomplish cool-down of the adsorbent solids leaving the final desorption zone with cross flow contact using a plurality of countercurrent contacts to hot regenerated adsorbent leaving the final impurity stage downwardly flowing for the transfer of heat to the reactivating gas leaving the regeneration section;

causing said heated gas to enter a heater for heating to the required temperature to accomplish sufficiently the desorption of impurities in the final desorption zone on a once through basis;

providing a regenerated adsorbent stream from said cool-down zone with sufficient cooling to remove the heat of wetting, preferably as a slurry with the final desorption liquid before introducing into the adsorber section; and

recirculating the cooled regenerated adsorbent stream for introduction into said adsorption section.

2. The method of treating as set forth in claim 1, wherein 96 weight percent or greater of the particulate adsorbents are in the 14 to 35 Tyler mesh range.

3. The method of treating as set forth in claim 1, wherein the liquid stream comprises a liquid olefinic hydrocarbon feedstream with a limited boiling range approximating less than 250 degrees centigrade for the 98 volume percent point with limited impurities less than approximately 12000 ppmw of sulfur to remove more than 98 weight percent of sulfur entering as feed, and the solids leaving the recycle liquid desorption zone generally are limited to less than 200 degrees centigrade, with the resulting regeneration section condensate containing most of the

olefin returned to the adsorption section to become part of the adsorber treated product.

5 4. The method of treating as set forth in claim 3, wherein any excessive dienes in the recycled liquid condensate from the recycle desorption zone of the regeneration section are hydrogenated selectively with a nickel or palladium containing catalyst, or other suitable catalyst, with limited hydrogen makeup, sufficiently moderate temperatures to avoid green oil formation or saturate olefins, and pressures below 300 psig before entering the adsorption section.

10 5. The method of treating as set forth in claim 1, wherein the liquid stream is a liquid hydrocarbon feed ranging from 3 to 15 in carbon numbers and the feed entering the adsorption section is not greater than 40 degrees centigrade and preferably below 20 degrees centigrade.

15 6. The method of treating as set forth in claim 1, wherein the liquid stream is a liquid hydrocarbon feed ranging from 3 to 15 in carbon numbers with a hydrogen containing gas as the reactivating medium makeup and having the vapors leaving the final desorption zone to enter a vapor phase reactor for the hydrogenation of most of the entering heteroatoms with the resulting reactor effluent being condensed with cooling to enter a separator wherein the heteroatom concentrated liquid is further separated.

20 7. The method of treating as set forth in claim 6, wherein the gas stream from the separator is treated for heteroatom removal and recycled as part of the reactivating gas to the cool down zone of the regenerator.

25 8. The method of treating as set forth in claim 6, wherein a limited amount of liquid is recycled from the regeneration section is generally less than 4 percent of the hydrocarbon fresh feed supplied to the adsorption section, and is stripped of light ends to fashion the mono aromatic concentrate normally boiling up to approximately 190 degrees centigrade separated as gasoline with possible recycle to the latter stages of the adsorption section for more complete sulfur removal.

30 9. The method of treating as set forth in claim 6, wherein most higher boiling residuals selected from the group consisting of naphthalene, unhydrogenated

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Sub-93 ant. benzothiophenes, and quinoline are separated by distillation with possible routing to a higher pressure hydrogenation unit such as a diesel hydrotreater.

5 10. The method of treating as set forth in claim 1, wherein the liquid stream is a hydrocarbon feed and the condensed liquid from the recycle liquid desorption zone is injected into the latter stages of the adsorption section.

11. The method of treating as set forth in claim 10, wherein the condensed liquid from the recycle zone is subjected to diene removal prior to being injected into the latter stages of the adsorption section.

10 12. The method of treating as set forth in claim 1, where the liquid stream is a hydrocarbon feed ranging from 3 to 15 in carbon numbers with the effluent vapors from the final desorption zone of the regeneration section being heat exchanged and cooled to produce a concentrated heteroatom liquid that may be biologically desulfurized or hydrogenated.

15 13. The method of treating as set forth in claim 1, wherein the adsorbent particles are spherical with the original adsorbent and makeup being predominantly greater than 10 Tyler mesh and less than 45 Tyler mesh, but with a particle diameter range of 1.5 for more than 96 percent of the particles.

20 14. The method of treating as set forth in claim 1, wherein a limited amount of a hydrogen containing gas is used as gas makeup to the first adsorption zone of the regenerator, while nitrogen or other suitable gas is used as the reactivating gas makeup to the cool-down zone of the regenerator.

15. The method of treating as set forth in claim 14, wherein total reactive gas makeup is less the 5% less than the reactive gas make up.

25 16. The method of treating as set forth in Claim 1, wherein the adsorber section comprises a limited number of fluidized stages by limiting the bed expansion in the fluidized zones of the adsorption section with less than seven meter settled bed height in the feed entry stage and less than thirty meter settled bed height in the final adsorption stage.

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5 17. The method of treating as set forth in claim 1, wherein the adsorber section comprises more than one adsorption vessel and the method comprises using part of the liquid adsorption stream from a preceding adsorption vessel closer to the fresh feed as a liquid lift for the withdrawn slurry from the succeeding vessel to reduce the pumping head required for the major part of the liquid adsorption stream that enters as feed to the succeeding vessel.

10 18. The method of treating as set forth in claim 1, wherein the method further comprises using an enlarged diameter at the top of the adsorber section to facilitate separation of the solids from the liquid while reducing the height for a given bed inventory in the top stage of an adsorption vessel and permitting lift liquid to be used without any increase in superficial velocity for the liquid in the fluidized beds below the enlarged diameter section.

15 19. The method as set forth in claim 1, wherein the method comprises using a suitable adsorbent vessel as a filtering medium for the fresh feed to ensure removal of scale or other possible debris from dirtier feeds, such as coker or visbreaker distillates, and to preclude nonregenerable poisons such as silicon compounds or iron from contaminating the circulating adsorbent used.

20 20. The method as set forth in claim 1, wherein the method comprises using screened, smaller diameter adsorbent solids discarded long term from the regenerator as a filtering medium for the fresh feed to be treated to ensure removal of scale and other possible debris or non-regenerable poisons from contaminating the circulating adsorbent used.

25 21. The method of treating as set forth in Claim 1, wherein the liquid stream is a hydrocarbon feed and the method comprises removing corrosive agents such as mercaptans below 0.5 ppmw for the adsorber treated product so that the product passes any copper strip or doctor test.

30 22. The method of treating as set forth in claim 1, wherein the liquid stream is a dirty, liquid hydrocarbon stream, such as a coker or visbreaker gasoline feedstream, and the method comprises producing a clear water-white product, free from any noxious odors as the adsorber treated product.

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23. The method of treating as set forth in claim 1, wherein the liquid stream is a liquid hydrocarbon feed and the method comprises removing nitrogen reduction to less than 0.3 ppmw nitrogen in the adsorber treated product.

5 24. The method of treating as set forth in claim 1, comprising a step of gravity transfer between stages of the adsorption vessel using a nuclear device for interface fluid level detection for the solids containing bed in a stage and control of the solids transfer by varying the opening in the conduit from the bottom such as with a pinch valve from the bed distributor of the upper stage that contains openings smaller than the fluidized particles which permit liquid effluent from the stage below
10 to enter the succeeding stage.

25. The method of treating as set forth in claim 24, wherein the slurry conduit enters below the near normal expanded solids bed height.

26. The method of treating as set forth in claim 24, wherein the differential for transfer of solids is provided by slurry density in the conduit versus clear liquid
15 density available below the upper stage distributor.

27. The method of treating as set forth in Claim 26, wherein the slurry conduit is located outside the adsorption vessel so that external access to the transfer valve is facilitated and interference with even, smooth distribution of the liquid entering the distributor above is minimal.

20 28. The method of treating as set forth in claim 1, wherein gravity transfers the solids in a continuous manner with a thin, cross-flow bed less than 0.5 meter in thickness for gas cross-flow with suitable baffling on the gas side and with controlled gas flow rates for gas cross-flow in the various zones of the regenerator to minimize the residence of solid particles subject to temperatures that may cause carbonation
25 deposits on the absorbent while avoiding reasorbtion in the desorption zones while avoiding readsorption due to significantly colder temperature of the particles at the gas outlet due to limited cross-flow bed length.

29. The method of treating asset forth in claim 1, wherein liquid feeds to the adsorber are cooled below ambient particularly for low impurity adsorber treated
30 product, such as below 5 ppmw sulfur, while treating any catalytic cracker full boiling

range gasoline or derived fractions, pyrolysis gasoline or other olefinic fresh feedstocks.

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30. A method of treating a liquid stream to remove impurities, where the impurities have a greater affinity for porous adsorbent particulates than do the components in the liquid, the method comprising the steps of:
5 flowing the liquid stream upwardly through a first upright adsorber vessel that contains the porous adsorbent particulates at a flow rate sufficient to establish fluidized bed performance between the porous adsorbent particulates and the liquid stream, the porous adsorbent particulates comprised of a 8 to 48 Tyler
10 mesh range with a size distribution that permits bed expansion no greater than 10 percent;
contacting the liquid stream with the porous adsorbent particulates during the flowing step with sufficient residence time for impurity adsorbance that removes impurities in the liquid stream to produce both a purified liquid stream that has
15 a reduced impurity concentration and an impurity-bound adsorbent;
discharging the purified liquid stream from the adsorber vessel;
withdrawing the impurity-bound adsorbent in a slurry from the first upright adsorber vessel;
processing the impurity-bound adsorbent after the withdrawing step to remove
20 impurities therefrom and produce a regenerated adsorbent; and
recycling at least a portion of the regenerated adsorbent through the adsorber vessel.

31. In a facility for use in removing impurities from a liquid stream by contacting the liquid stream with an adsorbent in an adsorber vessel and removing impurities from the adsorbent by the action of a regenerator vessel precedent to
25 recycling of the adsorbent through the adsorber vessel, the improvement comprising:
the adsorber vessel containing porous adsorbent particulates comprised of a 8 to 48 Tyler mesh range with a size distribution and configured for establishing fluidized bed performance with bed expansion no greater than 10 percent.